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(54) PRODUCTION OF LOWER OLEFIN

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the formation of a by-product at an industrially advantageous low temperature and efficiently produce the objective compound in high selectivity by using a catalyst containing a specific amount of a rare earth element supported on a zeolite when catalytically cracking a hydrocarbon.

SOLUTION: A $\geq 2C$ hydrocarbon raw material is brought into contact with a catalyst supporting a rare earth element in an amount of 0.4-20 expressed in terms of atomic ratio to the aluminum in a crystalline aluminosilicate zeolite thereon. The hydrocarbon raw material is preferably subjected to dehydrogenating treatment and then brought into contact with the catalyst to improve the yield. ZSM-5 or ZSM-11 or both are preferred as the zeolite.

Lanthanum, cerium and the like are preferred as the rare earth element. The catalyst preferably further contains 0.1-10 wt.% phosphorus supported thereon. The catalytic cracking reaction is preferably carried out in the presence of steam at 600-700°C.

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CLAIMS

[Claim(s)]

[Claim 1]Contact with a carbon numbers of two or more hydrocarbon raw materials for a catalyst, and are in charge of manufacturing lower olefin, A manufacturing method of lower olefin which makes a catalyst crystalline aluminosilicate zeolite which supported a rare earth element and in which a holding amount of a rare earth element of this catalyst is characterized by being the range of 0.4-20 in an atomic ratio to aluminum in zeolite.

[Claim 2]A manufacturing method of the lower olefin according to claim 1 whose crystalline aluminosilicate zeolite is ZSM-5 type and/or ZSM-11 type zeolite.

[Claim 3]A manufacturing method of the lower olefin according to claim 1 or 2 in which this catalyst contains further 0.1 to 10% of the weight of Lynn.

[Claim 4]A manufacturing method of the lower olefin according to claim 1 to 3 which performs a catalytic reaction under coexistence of a steam.

[Claim 5]A manufacturing method of the lower olefin according to claim 1 to 4 which performs a catalytic reaction by passing a catalyst bed including this catalyst after passing a dehydrogenation process for with a carbon numbers of two or more hydrocarbon raw materials.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In this invention, catalytic cracking of the hydrocarbon raw materials is carried out using a catalyst.

Therefore, it is related with lower olefin and the method of mainly manufacturing ethylene and propylene.

[0002]

[Description of the Prior Art]Lower olefin, such as ethylene and propylene, is substances important as basic materials of various chemicals articles. Conventionally, as a manufacturing method of these lower olefin, liquid hydrocarbon, such as gaseous hydrocarbon, such as ethane, propane, and butane, or naphtha, is used as a raw material, and the method of decomposing thermally under a steam atmosphere in the tubular furnace of an outside heat type is enforced widely. however, the thing for which a not less than 800 °C elevated temperature is needed in this method in order to raise olefin yield -- moreover -- therefore, it has the economically disadvantageous point that an expensive device material must be used. For this reason, the catalytic cracking method of hydrocarbon using a catalyst has been examined variously. Since it can decompose at low temperature (350-700 °C) comparatively when solid acid, especially zeolite are used also in them, many examples are reported. For example, in a series of patents of Asahi Chemical Industry Co., Ltd. (JP,60-222428,A, JP,61-7218,A, JP,3-130236,A, JP,6-192134,A, JP,6-192135,A, JP,6-199707,A, JP,6-228017,A, JP,6-346062,A, etc.). Although the catalytic cracking method of n-hexane and naphtha using the ZSM-5 type catalyst which controlled acidity and acid strength in the specific range is indicated, by this method, many aromatic components (benzene, toluene, xylene, following BTX) cannot generate, and an olefin cannot be obtained efficiently. Although catalytic cracking by ZSM-5 which controlled alpha value which is an index of cracking activity in the specific range by JP,1-213240,A and JP,3-504737,A is indicated, Many BTXs generate also with these catalysts and the olefin yield of $C_2 - C_4$ is about 40% or less than it. In JP,2-1413,A and JP,2-184638,A, the catalytic cracking method of the paraffin by ZSM-5 catalyst which supported

copper, cobalt, silver, etc. is indicated. Although it is reported by this method that propylene is obtained with the yield of 40 to 60%, it is data of the pulse reaction under the conditions diluted dramatically, and difficulty follows on commercial operation. The yield of ethylene is also as low as 20% or less. Many catalytic cracking by the catalyst which embellished ZSM-5 with other ingredients, for example, a rare earth element etc., is also reported. Although the catalytic cracking method of the paraffin by ZSM-5 catalyst which contains the rare earth element of 0.01-0.3 by the ratio of an atomic number to aluminum in ZSM-5 is indicated by U.S. Pat. No. 5,232,675 and No. 5,380,690, and European patent No. 727,404, Ethylene yield is 10% or less, propylene yield is 20% or less, and there is much generation of a liquefied ingredient rather. When hydrocarbon containing many unsaturated ingredients like [until now] butene, pentenes, and hexenes is contacted to zeolite, it is reported that the aromatic series containing BTX generates so much (for example, JP,56-42639,B, JP,4-5712,B, and U.S. Pat. No. 3,845,150.) U.S. Pat. No. 3,960,978 of the yield of light olefins, such as ethylene propylene, etc. were low when it was going to disassemble hydrocarbon containing an unsaturated ingredient. Metal oxide catalysts other than zeolite. many methods of the olefin production by decomposition of the used paraffin are also reported (for example, JP,48-13523,B, JP,46-25370,B, JP,49-45364,B, JP,52-12162,B, JP,53-23806,B, JP,56-5435,B, and JP,56-5436,B.) JP,56-29919,B, JP,60-41054,B, etc. However, in these examples, generally decomposition temperature is equivalent (not less than 700-800 **) with the present thermal decomposition method, and there is a problem that carbon monoxide and carbon dioxide generate mostly. As mentioned above, the method of disassembling light hydrocarbon using a catalyst and manufacturing an olefin especially ethylene, and propylene efficiently is not established.

[0003]

[Problem(s) to be Solved by the Invention]When this invention carries out catalytic cracking of the hydrocarbon raw materials using a catalyst, it controls generation of by-products, such as aromatic hydrocarbon and a heavy thing, and makes it the technical problem to provide the method of manufacturing lower olefin, such as ethylene and propylene, efficiently.

[0004]

[Means for Solving the Problem]This invention persons are advantageous low temperature industrially by carrying out catalytic cracking of the hydrocarbon raw materials using a catalyst which supported a rare earth element of quantity of a specific range to zeolite, as a result of advancing research wholeheartedly that said technical problem should be solved, Generation of by-products, such as aromatic hydrocarbon and a heavy thing, was controlled, it found out that ethylene and propylene could be manufactured on a high selection target, and this invention was completed. That is, according to this invention, a manufacturing method of lower olefin carrying out catalytic cracking of the hydrocarbon raw materials using a zeolite catalyst which supported a rare earth element of quantity of a specific range is provided.

[0005]

[Embodiment of the Invention]As hydrocarbon raw materials used by this invention, hydrocarbon gaseous or liquefied at ordinary temperature and ordinary pressure can be used.

Generally, the carbon numbers 2-30 and the hydrocarbon raw materials which make paraffin of 2-20 or this preferably the main ingredients (more than 10wt%) are used. As such hydrocarbon raw materials, light hydrocarbon fractions, such as paraffin, such as ethane, propane, butane, pentane, and hexane, or naphtha, and gas oil, can be mentioned, for example. A raw material component is not limited to saturated hydrocarbon, and can also use the thing containing the ingredient which has an unsaturated bond. The aromatic component may be contained. The point that BTX-ization can be controlled and ethylene propylene can be obtained with high yield also by the fraction containing an unsaturated ingredient is one of the features of this catalyst. For this reason, higher ethylene propylene yield is obtained by decomposing the fraction after passing through the dehydrogenation process of many [for an unsaturation] fraction, or paraffin with this catalyst rather than decomposing paraffin with this catalyst as it is. As a catalyst used by the dehydrogenation process before the decomposition process in this catalyst, an ulmin acid zinc catalyst etc. are mentioned at the time of an alumina catalyst, platinum, and **** at the time of chromia **, for example.

[0006]The catalyst of this invention uses as the main ingredients the zeolite which supported the rare earth element. As zeolite, the zeolite especially ZSM-5, and/or ZSM-11 of a high silica type are preferred. SiO_2 / aluminum₂O₃ ratio of zeolite -- 25-800 -- it is 50-600 preferably and is 100-300 still more preferably. Although it is usable in anythings as a rare earth element, a lantern, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, etc. can be mentioned preferably. Each may be alone used for a rare earth element, or two or more sorts may be mixed and used for it. A catalyst can be easily prepared by impregnating and calcinating [dry and] proton type zeolite in solutions in which various salts of a rare earth element, for example, acetate, a nitrate, a halogenide, sulfate, carbonate or an alkoxide, acetylacetonate, etc. were dissolved, such as water and ethanol. Although some rare earth elements enter in zeolite fine pores by these supporting methods and ionic exchange of the part is carried out to the proton of zeolite, on zeolite, most serves as an oxide and is supported. Being supported on zeolite is important for a rare earth element, and the effect of this catalyst is not acquired only by mixing a rare earth oxide with zeolite physically.

[0007]In the catalyst of this invention, the holding amount of a rare earth element, as opposed to aluminum in zeolite -- an atomic ratio -- 0.4-20 -- desirable -- 1-10 -- it being 2-5 still more preferably, and, When there are few holding amounts than these values, generation of aromatic hydrocarbon and a heavy thing is not controlled, but since catalytic activity falls rapidly when there are too many holding amounts, olefin yield decreases. Although the effect of a rare earth element is not yet clear, since activity is not acquired when an acid site is supported to Silicalite which it has, as shown in the after-mentioned example, according to the operation condition of this invention, the rare earth element (oxide) itself is considered to be inertness to disassembly of hydrocarbon. It is surmised that, as for the decomposition reaction, the acid site of zeolite is the active spot from this, a rare earth element (oxide) probably promotes desorption from the zeolite of the generated olefin by the basic operation, and the aromatic series as a side reaction and generation of the heavy thing are controlled as a result. [0008]The shape in particular of the catalyst of this invention may not be limited, but the thing

of which shape, such as powder and mold goods, may be sufficient as it. Lynn can be supported by impregnating diammonium-hydrogen-phosphate solution in this catalyst which Lynn has an effect in the durability enhancement of a catalyst also in these, for example, supported the rare earth element. As for Lynn, it is preferably preferred to this catalyst to make it contain two to 5% of the weight still more preferably one to 7% of the weight 0.1 to 10% of the weight. The ingredient of others [catalysts / these] other than zeolite and rare earth, for example, alkali, an alkaline earth, a transition metal, the precious metals, halogen, Lynn, a binder, etc. may be contained further again. It is also possible to use it, mixing with bulking agents, such as silica, alumina, magnesia, or quartz sand.

[0009]The reactor of the form of the fixed bed, a fluid bed, etc. is used for the catalyzed degradation of this invention, and it is performed by supplying hydrocarbon raw materials to the catalyst bed filled up with the above-mentioned catalyst. Hydrocarbon raw materials may be diluted with nitrogen, hydrogen, helium, or steam at this time. especially steam has an effect which maintains the active state of a catalyst also in these diluents, and the amount of supply of desirable steam receives coal-for-coke-making-ized hydrogen -- 0.1 - 1wt% -- it is 0.3 - 0.7wt% still more preferably. The range of 350-780 ** of reaction temperature [500-750 ** of] is 600-700 ** still more preferably preferably. Although it can carry out also at the temperature over 780 **, generation of methane and Cork increases rapidly. Since activity sufficient at less than 350 ** is not acquired, the olefin yield per passage decreases once. Although either under ordinary pressure, decompression, or application of pressure can carry out reaction pressure, application of pressure is usually adopted a little from ordinary pressure. If the method of this invention is enforced under the above conditions, as compared with the conventional thermal decomposition method, hydrocarbon raw materials can be efficiently disassembled at low temperature, and lower olefin, such as ethylene and propylene, can be manufactured selectively.

[0010]

[Example]Although an example is given to below and this invention is explained to it still in detail, this invention is not limited to these examples.

[0011]proton type ZSM-5 aluminosilicate (SiO_2 / aluminum $_2\text{O}_3$ mole ratio 200 measured by

cay light X-ray analysis, and BET surface area $360\text{m}^2/\text{g}$.) powdered as example 1 zeolite Acetic acid lantern solution containing the 0.4-g lantern which is equivalent to the 10wt% in the 150-micrometer or less particle diameter of 4 g [What dissolved acetic acid lantern 1 / 2 0.9877-g hydrate ($\text{La}(\text{CH}_3\text{COO})_3$ and $0.5\text{H}_2\text{O}$) in 60 cc of deionized water] was impregnated, and it agitated at 40 ** for 1 hour. Moisture was evaporated over about 2 hours under decompression of the generated slurry, agitating at 40 ** - 60 **, and white powder was obtained. Among the air, 120 **, after drying for 8 hours, temperature up of the obtained powder was carried out to 600 ** over 4 hours in the muffle furnace, and it was calcinated at 600 ** for 5 hours. What ground the obtained white solid with the mortar and passed a 150-micrometer sieve was made into 10%La/ZSM-5 catalyst (La/aluminum atomic ratio =4.3). The coil made from quartz (with an outer diameter of 4 mm with the interpolation pipe for thermo couples) 10 mm in inside

diameter and 330 mm in length was filled up with 1 g of this catalyst with the inert filler (quartz sand) so that the length of a catalyst bed might be set to about 70 mm. The upper and lower sides of the catalyst bed were filled up with quartz sand. Temperature up of the temperature of a catalyst bed was carried out to 650 **, passing air to this reactor by 40 cc/min (it is [0 **, 1 atmosphere conversion, and the following] the same), and pretreatment was performed as it was for 1 hour. The temperature of the catalyst bed was held at 650 ** after the end of pretreatment, 2.8 cc/min, nitrogen, and steam were supplied for normal butane by the flow of 5.7 cc/min and 0.01 g/min as a raw material, respectively, and catalyzed degradation of normal butane was performed. Gas chromatography analyzed the resultant and output yield and a raw material inversion rate were computed with the following formula.

Output yield (% of the weight) = (each ingredient weight / feed weight) x100
 raw-material inversion rate (%) =(1-unreacted raw material weight / feed weight) x100
 reaction result is shown in Table 1.

[0012]proton type ZSM-5 aluminosilicate (SiO_2 / aluminum $_2\text{O}_3$ mole ratio 200 measured by cay light X-ray analysis, and BET surface area $360\text{m}^2/\text{g}$.) powdered by the same method as comparative example 1 Example 1 The catalyst which supported the lantern equivalent to the 0.5wt% was prepared to the particle diameter of 150 micrometers or less, and it was made it with 0.5%La/ZSM-5 catalyst (La/aluminum atomic ratio =0.22). Catalyzed degradation of normal butane was performed by the same method as Example 1 using 1 g of this catalyst. A reaction result is shown in Table 1. When a rare earth holding amount is too low so that it may understand in this example, there are many BTXs, and olefin yield is low.

[0013]the comparative example 2 -- proton type ZSM-5 powdered aluminosilicate (SiO_2 / aluminum $_2\text{O}_3$ mole ratio 200 measured by cay light X-ray analysis, and BET surface area $360\text{m}^2/\text{g}$.) Made the particle diameter of 150 micrometers or less into the catalyst as it was, and it was filled up with it 1g, and also catalyzed degradation of normal butane was performed on the same conditions as Example 1. A reaction result is shown in Table 1. BTX generates many catalysts which are not supporting the rare earth element, and ethylene and propylene yield are low so that it may understand in this example.

[0014]Silicalite (SiO_2 , BET surface area $360\text{m}^2/\text{g}$, particle diameter of 150 micrometers or less) was used instead of comparative example 3 proton type ZSM-5 aluminosilicate, impregnating support of the lantern was carried out by the same method as Example 1, and 10%La / Silicalite catalyst was prepared. The decomposition reaction of normal butane was performed on the same conditions as Example 1 using 1 g of this catalyst. A reaction result is shown in Table 1. With the catalyst which supported the rare earth element to Silicalite without a solid acid point, decomposition activity is not obtained so that it may understand in this example.

[0015]

[Table 1]

番 号	実施例 1	比較例 1	比較例 2	比較例 3
触 媒	10%La/ZSM-5	0.5%La/ZSM-5	HZSM-5	10%La/ZSM-5
La/Al原子比	4.3	0.22	0.0	---
原 料	n-ブタン	n-ブタン	n-ブタン	n-ブタン
温 度	650℃	650℃	650℃	650℃
原料転化率(%)	98.5	97.0	97.5	6.9
生成物収率 (対原料重量%)				
エチレン	30.8	24.4	25.0	2.0
プロピレン	18.3	14.2	12.9	3.1
ブテン類	4.6	3.7	3.5	0.0
1,3-ブタジエン	0.1	0.0	0.0	0.0
BTX	2.9	16.8	18.1	0.0
メタン	15.1	12.9	13.8	1.2
エタン	18.4	17.6	17.5	0.3
プロパン	3.2	2.5	2.1	0.0
ブタン類	1.8	3.2	2.7	63.1
C ₅ +, コーク	1.3	2.2	2.4	0.0
一酸化炭素	1.7	1.1	1.0	0.0
二酸化炭素	7.3	1.0	0.2	0.1
エチルメタセレン	49.1	38.6	37.9	5.1
C ₆ ~C ₁₀ オレフィン	53.8	42.3	41.4	5.1

[0016]Example 2, Example 3 and the comparative example 4, and the comparative example 5 -- it is shown that a difference remarkable in ethylene propylene yield and BTX yield comes out of the example of these by the case of 0.4 or more and 0.3 or less by an atomic ratio to aluminum in zeolite in a rare earth holding amount. The 10%La/ZSM-5 catalyst same as a catalyst as Example 1 (La/aluminum atomic ratio =4.33), and 1%La/ZSM-5 catalyst (La/aluminum atomic ratio =0.43) prepared like Example 1 -- it was filled up with 0.5 g with the inert filler (quartz sand), respectively so that the length of a catalyst bed might become the same coil as Example 1 with about 50 mm. Temperature up of the temperature of a catalyst bed was carried out to 650 **, passing air by 40 cc/min to this reactor, and pretreatment was performed as it was for 1 hour. The temperature of the catalyst bed was held at 650 ** after the end of pretreatment, 2.8 cc/min, nitrogen, and steam were supplied for normal butane by the flow of 12.2 cc/min and 0.0047 g/min as a raw material, respectively, and catalyzed degradation of normal butane was performed. It is shown in Table 2 by making this result into Example 2 and Example 3. Catalyzed degradation of normal butane was performed on the same conditions as Examples 2-3 using the 0.5%La/ZSM-5 [still more nearly same] as the thing of the comparative example 1 as a catalyst catalyst (La/aluminum atomic ratio =0.22), and HZSM-5 catalyst which is not supported [same] as the comparative example 2. It is shown in Table 2 by making this result into the comparative example 4 and the comparative example 5. If a La/aluminum atomic ratio is reduced or less to 0.4 to 0.3 so that clearly [in Table 2], generation of BTX will increase remarkably and ethylene propylene yield will decrease.

[0017]

[Table 2]

番 号	実施例2	実施例3	比較例4	比較例5
触 媒	10%La/ZSM-5	1%La/ZSM-5	0.5%La/ZSM-5	10ZSM-5
La/Al原子比	4.3	0.43	0.22	0.0
原 料	n-ブタン	n-ブタン	n-ブタン	n-ブタン
温 度	650℃	650℃	650℃	650℃
原料転化率(%)	95.5	96.2	95.5	94.0
生成物収率 (対原料重量%)				
エチル+プロピル	50.0	50.3	49.4	41.6
BTEX	6.4	7.1	13.2	13.0

[0018]Example 4 -- this example shows the catalyzed degradation by the catalyst which added Lynn to the catalyst of Example 1 further. The diammonium-hydrogen-phosphate solution (what dissolved the diammonium hydrogen phosphate 0.1706g in 20 g of deionized water) which includes 0.02-g Lynn equivalent to 2wt% of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. in 2 g of 10%La/ZSM-5 catalysts prepared in Example 1 was impregnated, and it agitated at 40 °C for 1 hour. Moisture was evaporated over about 2 hours under decompression of the generated slurry, agitating at 40 °C - 60 °C, and white powder was obtained. Among the air, 120 °C, after drying for 8 hours, temperature up of the obtained powder was carried out to 600 °C over 4 hours in the muffle furnace, and it was calcinated at 600 °C for 5 hours. What ground the obtained white solid with the mortar and passed a 150-micrometer sieve was made into 10%La-2%P/ZSM-5 catalyst. (La/aluminum atomic ratio =4.3)

1 g of this catalyst was used and the same reaction as Example 1 was carried out. A reaction result is shown in Table 3.

[0019]the proton type ZSM-5 same powdered aluminosilicate (SiO_2 / aluminum₂O₃ mole ratio 200 measured by cay light X-ray analysis, and BET surface area360m²/g.) as what was used in comparative example 6 Example 1 The diammonium-hydrogen-phosphate solution (what dissolved the diammonium hydrogen phosphate 0.3411g in 40 g of deionized water) which includes 0.08-g Lynn equivalent to 2wt% of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. in the 150-micrometer or less particle diameter of 4 g was impregnated, and it agitated at 40 °C for 1 hour. Moisture was evaporated over about 2 hours under decompression of the generated slurry, agitating at 40 °C - 60 °C, and white powder was obtained. Among the air, 120 °C, after drying for 8 hours, temperature up of the obtained powder was carried out to 600 °C over 4 hours in the muffle furnace, and it was calcinated at 600 °C for 5 hours. What ground the obtained white solid with the mortar and passed a 150-micrometer sieve was made into 2%P/ZSM-5 catalyst. 1 g of this catalyst was used and the same reaction as Example 1 was carried out. A reaction result is shown in Table 3. With the catalyst which made only Lynn support so that it may understand in this example, olefin yield is low.

[0020]

[Table 3]

番 号	実施例 4	比較例 6
触 媒	La-P/ZSM-5	F-ZSM-5
原 料	n-ブタン	n-ブタン
温 度	650℃	650℃
原料転化率(%)	93.7	29.1
生成物収率 (対原料重量%)		
エチレン	28.1	5.3
プロピレン	20.9	7.6
ブテン類	5.3	3.1
1,3-ブタジエン	0.0	0.0
BTX	3.2	0.1
メタン	12.2	3.1
エタン	17.8	4.2
プロパン	1.8	0.2
ブタン類	6.3	75.9
C ₅ +, コーク	2.0	0.2
一酸化炭素	1.2	0.0
二酸化炭素	1.5	0.0
エチルメグロシン	45.0	12.9
C ₂ ~C ₆ オレフィン	54.3	16.0

[0021]and also it used cerium acetate 1 hydrate, nitric acid praseodymium 6 hydrate, and acetic acid samarium 4 hydrate instead of Example 5 - 7 acetic-acid lantern 1 / 2 hydrate, respectively -- the same method as Example 1 -- a rare earth element -- 10wt% -- the supported catalyst was prepared. (Atomic ratio: Ce/aluminum=4.3, Pr/aluminum=4.3, Sm/aluminum=4.00)

The coil made from quartz (with an outer diameter of 4 mm with the interpolation pipe for thermo couples) 10 mm in inside diameter and 330 mm in length was filled up with 0.5 g of these catalysts with the inert filler (quartz sand), respectively so that the length of a catalyst bed might be set to about 50 mm. The upper and lower sides of the catalyst bed were filled up with quartz sand. Temperature up of the temperature of a catalyst bed was carried out to 650 **, passing air by 40 cc/min to this reactor, and pretreatment was performed as it was for 1 hour. The temperature of the catalyst bed was held at 650 ** after the end of pretreatment, 2.8 cc/min, nitrogen, and steam were supplied for normal butane by the flow of 12 cc/min and 0.0047 g/min as a raw material, respectively, and catalyzed degradation of normal butane was performed. A result is shown in Table 4.

[0022]

[Table 4]

番 号	実施例 5	実施例 6	実施例 7
触 媒	10% La/ZSM-5	10% Pr/ZSM-5	10% Sm/ZSM-5
原 料	n-ブタン	n-ブタン	n-ブタン
温 度	650℃	650℃	650℃
原料転化率(%)	96.1	96.3	97.2
生成物収率 (対原料重量%)			
エチレン	30.1	30.4	30.4
プロピレン	19.2	19.8	19.0
ブテン類	4.3	4.3	4.0
1,3-ブジエン	0.0	0.0	0.1
BTX	6.5	4.7	5.9
メタン	12.4	13.8	13.9
エタン	17.3	17.2	17.5
プロパン	2.4	2.6	2.8
ブタン類	4.0	3.8	3.0
C ₅ +, コーク	1.4	1.0	0.9
一酸化炭素	1.9	1.1	1.2
二酸化炭素	1.5	4.4	3.9
ナフテン+ジナフテン	49.3	50.2	49.4
C ₉ ~C ₁₀ ナフテン	53.8	54.5	53.5

[0023]Example 8 -- this example shows the example of catalytic cracking of the saturation by a rare earth carried catalyst, and an unsaturation hydrocarbon mixture. The reactor was filled up with 0.5 g of 10%La/ZSM-5 catalysts prepared by the same method as Example 1 like Examples 5-7. Temperature up was carried out to 650 **, passing air by 40 cc/min to a reactor, and pretreatment was performed as it was for 1 hour. holding the temperature of a catalyst bed at 650 ** after the end of pretreatment -- as a raw material -- 1-butene -- 30vol% -- the included normal butane / 1-butene mixed gas 2.8 cc/min, Nitrogen and steam were supplied by the flow of 12 cc/min and 0.0047 g/min, respectively, and catalyzed degradation of normal butane / 1-butene mixed gas was performed. A result is shown in Table 5.

[0024]Example 9 -- this example shows the example of catalytic cracking of unsaturated hydrocarbon by a rare earth carried catalyst. The coil made from quartz (with an outer diameter of 4 mm with the interpolation pipe for thermo couples) 10 mm in inside diameter and 330 mm in length was filled up with 0.3 g of 10%La/ZSM-5 catalysts prepared by the same method as Example 1 with the inert filler (quartz sand) so that the length of a catalyst bed might be set to about 30 mm. The upper and lower sides of the catalyst bed were filled up with quartz sand. Temperature up of the temperature of a catalyst bed was carried out to 650 **, passing air by 40 cc/min to this reactor, and pretreatment was performed as it was for 1 hour. The temperature of the catalyst bed was held at 650 ** after the end of pretreatment, 1.8 cc/min, nitrogen, and steam were supplied for 1-butene by the flow of 15 cc/min and 0.0078 g/min as a raw material, respectively, and catalyzed degradation of 1-butene was performed. A result is shown in Table 5.

[0025]

[Table 5]

番 号	実施例 8	実施例 9
触 媒	10%La/ZSM-5	10%La/ZSM-5
原 料	ブテン/ブタン	1-ブテン
温 度	650℃	650℃
原料転化率(%)	95.4	95.7
生成物収率 (対原料重量%)		
エチレン	32.8	37.5
プロピレン	20.7	30.4
ブテン類	4.3	7.4
1,3-ブジエン	0.1	0.1
B T X	6.7	9.2
メタン	12.6	5.1
エタン	12.6	0.9
プロパン	2.7	1.8
ブタン類	2.6	0.9
C ₅ +, コーク	0.6	0.7
一酸化炭素	0.9	0.7
二酸化炭素	7.3	7.1
エチン+プロピン	53.5	67.9
C ₂ ~C ₄ オレフィン	57.9	74.4

[0026]Example 10 -- this example shows the example of catalytic cracking of the hexane by a rare earth carried catalyst. The coil made from quartz (with an outer diameter of 4 mm with the interpolation pipe for thermo couples) 10 mm in inside diameter and 330 mm in length was filled up with 0.5 g of 10%La/ZSM-5 catalysts prepared by the same method as Example 1 with the inert filler (quartz sand) so that the length of a catalyst bed might be set to about 50 mm. The upper and lower sides of the catalyst bed were filled up with quartz sand. Temperature up of the temperature of a catalyst bed was carried out to 650 **, passing air by 40 cc/min to this reactor, and pretreatment was performed as it was for 1 hour. The temperature of the catalyst bed was held at 650 ** after the end of pretreatment, as a raw material, 0.42 g/h, nitrogen, and steam were supplied by 2 cc/min and 0.0047 g/min, hydrogen was supplied for normal hexane by the flow of 11 cc/min, respectively, and catalyzed degradation of normal hexane was performed. A result is shown in Table 6.

[0027]proton type ZSM-5 aluminosilicate (SiO₂ / aluminum₂O₃ mole ratio 200 measured by cay light X-ray analysis, and BET surface area360m²/g.) powdered as comparative example 7 catalyst It was filled up with 0.5g of particle diameter of 150 micrometers or less, and also catalyzed degradation of normal hexane was performed on the same conditions as Example 10. A result is shown in Table 5. Thus, when the rare earth element is not being supported, there are many BTXs, and olefin yield is low.

[0028]Example 11 -- this example shows the example which filled up the preceding paragraph of the rare earth carried catalyst with the dehydrogenation catalyst, and performed catalytic cracking of paraffin. The coil made from quartz (with an outer diameter of 4 mm with the

interpolation pipe for thermo couples) 10 mm in inside diameter and 330 mm in length was filled up with 0.5 g of 10%Pr/ZSM-5 catalysts prepared by the same method as Example 6 with the inert filler (quartz sand) so that the length of a catalyst bed might be set to about 50 mm. The upper part of this catalyst bed was filled up with 3g of platinum system dehydrogenation catalysts (for example, thing of US5,344,805 statement), and that upper part and the lower part of the catalyst bed were further filled up with quartz sand. Passing air by 40 cc/min to this reactor, temperature up of the catalyst bed with which 10%Pr/ZSM-5 catalyst was filled up into the catalyst bed with which the dehydrogenation catalyst was filled up to 580 °C was carried out to 650 °C, and it performed pretreatment as it was for 1 hour. The temperature of a catalyst bed is held at 580 °C and 650 °C as it is after the end of pretreatment, As a raw material, 2.8 cc/min, nitrogen, and steam were supplied by 2 cc/min and 0.0078 g/min, hydrogen was supplied for normal butane by the flow of 11 cc/min, respectively, and catalyzed degradation of normal butane was performed. A result is shown in Table 6.

[0029]

[Table 6]

番 号	実施例10	比較例 7	実施例 11
触 媒	10%La/ZSM-5	10%ZSM-5	脱水素触媒 +Pr/ZSM-5
原 料	n-ヘキサン	n-ヘキサン	n-ブタン
温 度	650℃	650℃	580℃～650℃
原料転化率(%)	100.0	99.8	68.0
生成物収率 (対原料重量%)			
エチレン	30.1	27.0	34.7
プロピレン	19.2	17.9	21.0
ブテン類	4.1	4.4	4.0
1,3-ブジエン	0.1	0.0	0.1
BTX	9.4	16.4	6.7
メタン	10.4	7.6	11.4
エタン	13.5	13.0	9.6
プロパン	8.6	8.3	3.3
ブタン類	0.9	1.0	2.4
C ₅ +, コーク	1.1	2.1	0.7
一酸化炭素	3.3	0.0	3.6
二酸化炭素	2.3	0.9	8.4
エチル+プロピル	49.3	44.9	55.7
C ₃ ～C ₆ オレフィン	53.5	49.3	59.8

[0030]Example 12 -- this example shows the data about the endurance of a rare earth carried catalyst. 1 g of catalysts prepared by the same method as Example 2 were used, and it reacted on the same conditions as Example 1. The reaction result of 4 hours after 1 hour after a reaction start and a reaction start is shown in Table 7. Thus, remarkable degradation was not accepted with this catalyst.

[0031]proton type ZSM-5 aluminosilicate (SiO₂ / aluminum₂O₃ mole ratio 200 measured by

cay light X-ray analysis, and BET surface area $360\text{m}^2/\text{g}$.) powdered as comparative example 8 catalyst The same reaction as Example 10 was carried out using the 150-micrometer or less particle diameter of 1 g. The reaction result of 4 hours after 1 hour after a reaction start and a reaction start is shown in Table 7. Thus, with the catalyst which is not supporting rare earth, olefin yield is low and degradation's is early.

[0032]

[Table 7]

番 号	実施例12	比較例 8			
触 媒 原 料 温 度	La-P/ZSM-5 n-ブタン 650℃	H-ZSM-5 n-ブタン 650℃			
原料転化率(%)	1時間	4時間	1時間	4時間	
原料転化率(%)	93.5	91.7	95.8	74.2	
生成物収率 (対原料重量%)					
エチレン	26.3	26.2	25.3	15.5	
プロピレン	20.7	20.2	13.8	15.5	
ブテン類	5.5	6.0	3.5	4.7	
1,3-ブジエン	0.0	0.1	0.0	0.0	
B T X	3.4	3.9	16.6	5.7	
メタン	12.1	11.7	12.8	9.7	
エタン	17.7	17.5	16.6	13.8	
プロパン	1.9	2.0	2.0	1.7	
ブタン類	6.5	8.5	4.4	25.0	
C ₅ +、コーク	1.7	2.5	2.5	1.7	
一酸化炭素	1.3	0.9	1.0	0.4	
二酸化炭素	1.4	0.9	0.2	0.1	
エチン+プロリン	49.0	46.4	39.1	34.0	
C ₂ + C ₃ + プロリン	54.5	52.5	42.6	38.7	

[0033]

[Effect of the Invention]According to the method of this invention, a gas or liquid hydrocarbon can be used as a raw material, generation of by-products, such as aromatic hydrocarbon and a heavy thing, can be controlled, and lower olefin, such as ethylene and propylene, can be manufactured selectively. In the case of this invention, as compared with the conventional decomposing method, it is possible to reduce reaction temperature by not less than 100 **.

[Translation done.]